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Improving catalytic sensors performances by electronic techniques

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ABSTRACT

The sensor used in French mines to detect firedamp (methane) in airways is a platinum filament catalytic sensor.

Its performance characteristics have been constantly improved by new conditioning techniques : heating filaments functioning at high temperature, signal processing.

In this document, we describe the operation of the sensor and the conditioning techniques successively used in different mine gas detectors, stressing for each the improved performance obtained.

In conclusion, we will show that the last technique recently developed broadens the field of use of the sensor to industrial and domestic explosimetry.

INTRODUCTION

Sensors used in explosimeters for the detection of explosive gases are generally catalytic. The most widespread are catalytic pellets.

A metallic oxidation catalyst is heated to a sufficiently high temperature to oxidize the gas. The oxidation reaction increases the temperature of the catalyst which increases its electrical resistance, whose amplitude is proportional to the gas concentration.

In the 1950s we developed a sensor of this type for the mining industry. It was based on a platinum filament and destined to detect methane, responsible for mine explosions.

The filament is distinguished from the catalytic pellets by its operating temperature : 1000°C instead of 600°C, which confers on it the advantage of being relatively insensitive to fouling and catalyst poisoning. The disadvantage, however, is rapid wear, preventing it from operating permanently.

The measurement technique thus involves energizing the sensor just long enough to make the measurement and then turning it off for as long as the application permits.

The first instruments of this time could run for 100,000 measurements, or about 9 months at the rhythm of one measurement every 4 minutes.

By improving the filament heating technique, the measurement capacity has been increased considerably : 10,000,000 measurements with the last methanemeter recently marketed, or a lifetime of 1.5 years at the practically continuous measurement rhythm of once every 5 seconds.

Endowed with these performance characteristics, the platinum filament sensor is today a reliable solution for explosimetry, in particular in environments polluted with certain catalyst poisons such as sulfur-containing products, which other catalytic sensors resist poorly.

In addition, the technique involving brief heating pulses, applicable only to filament sensors since it requires a very low thermal inertia of the sensor, has enabled new procedures to be developed for the identification of certain combustible gases or vapors and for the measurement of methane concentrations up to 100% v/v.

1. DESCRIPTION OF THE SENSOR (figure 1)

It is composed of two spiral filaments made of pure platinum : a detector filament and a compensating filament, both 80 μm in diameter but of unequal lengths.

The filaments are enclosed inside a hemispherical chamber made of sintered metal, enabling the natural diffusion of gases. They are welded to massive high thermal inertia antennas, that emerge from the chamber through isolated ports.

An activated charcoal filter inside the chamber surrounds the filaments and protects them from catalyst poisons, in particular silicones.

2. OPERATION

2.1 Detector filament

During the measurement period, a current I passes through the filament, raising its temperature in the center to 1000°C by the Joule effect.

Its electrical resistance R_d is a function of temperature T , which depends on I and on the quantities of oxidized gases.

The temperature of the filament is not the same along its entire length because of the cooling caused by the metallic supports.

Catalytic activity occurs on the central spires, whose temperature is higher than 800°C (figure 2).

The detector filament is appropriately treated to eliminate impurities in platinum.

Its temperature is determined in order for catalytic activity to be maximal at low methane concentrations, lower than the L.I.E., and to burn off products that could foul its surface, thereby reducing the active sites on which the oxidation occurs.

2.2 Compensating filament

This filament does not undergo a purifying treatment and is heated at a lower temperature, about 600°C on the central spires. At this temperature, catalytic activity starts at the stoichiometric concentration of 10% v/v for methane.

The compensator has a dual role : it compensates the thermal effects that interfere with detector measurement (temperature and thermal conductivity of the ambient medium), and detects high levels to remove any doubts concerning detector measurement (figure 3).

$$R_c(600^\circ\text{C}) = 0.73 \, \Omega, R_c(0^\circ\text{C}) = 0.29 \, \Omega$$

3. CHARACTERISTICS

3.1. Lifetime

Sensor lifetime is that of the detector filament. Platinum wear begins at 600°C and is particularly high around the operating temperature of the filament (at temperatures close to 1000°C, the rate of wear of the platinum filament is proportional to the cube of temperature). It is thus desirable to control this temperature throughout filament life, in particular when there is a supply of additional heat resulting from the oxidation of a gas.

Filament wear, greater in the central zone, results in a reduction in the cross-section of the wire, increasing resistance when cold $R_d(0^\circ\text{C})$ and when hot $R_d(T)$. This increases the explosimeter readings by a constant quantity and thus requires frequent recalibration of apparatus zero (reading in pure air).

Sensor lifetime thus depends on the duration of the measurement and on filament temperature during the measurement.

The various heating techniques used in several generations of methane detectors in order to increase lifetime have attempted to reduce the duration of the measurement and to control temperature.

3.2 Response time of the methane detector (figure 4)

The response time of a methane detector or an explosimeter is the time it takes to indicate 90% of the value of a concentration of gas G.

The response time of the instrument depends on :

- the response time of the sensor (T_{sens}), which is the time the gas takes to fill in the combustion chamber,
- the extinction time (T_{ext}) separating two consecutive measurements,
- the occurrence of the measurement in relation to the gas concentration.

If $T_{ext} > T_{sens}$ then : $T_{sens} < \text{response time} < T_{sens} + T_{ext}$

3.3 Electric consumption

W_{meas} = energy consumed during the measurement =

$$(R_d \times I_d^2 + R_c \times I_c^2) \times T_{heat}$$

P_{meas} = power dissipated during the measurement = $R_d \times I^2$

P_{mean} = mean power = $P_{meas} \times T_{heat} / (T_{heat} + T_{ext})$

Mean power takes into account the extinction time of the filament. It determines battery autonomy for portable apparatus.

T_{heat} = filament heating time = duration of measurement

T_{ext} = duration of filament extinction

4. HEATING TECHNIQUES AND PERFORMANCES

A number of different techniques have been used since the creation of the sensor, as developments in electronic components made them possible. We will describe them in the chronological order of development of the methane detectors that used them.

4.1 Constant intensity heating (figure 5) : remote mine gas detector CTT63/40, GTM mine gas detector

Since the sensor can be placed at a distance from the measurement device, this heating mode was chosen to overcome voltage drops in the cable and in the contacts.

It has a classical bridge structure. A constant intensity 0.74 A current passes through the filaments and raises them to operating temperature in about 1.5 seconds. The zero potentiometer is used to adjust U_b to offset the shift caused by sensor wear.

When a gas is oxidized on the detector, R_d increases, U_a increases more than U_b , and the measurement signal ($U_a - U_b$) increases : about 50 mV per % volume CH_4 . Measurement time is defined as the time the operator requires to read the galvanometer display.

Constant current heating offers a very low measurement capacity, with an excessively long response time. The measurement rhythm of methane detectors operating according to this principle was set at 4 minutes in order to obtain an acceptable compromise between response time, sensor lifetime (9 months) and the frequency of recalibration (weekly).

Filament temperature, proportional to $R_d(T) \times I^2$, increases with increasing filament wear. Wear is also considerably accelerated by gas oxidation: the heat supplied by the current is supplemented by those arising from the oxidation reaction : these instruments have a life time of only 30,000 measurements in 2% v/v CH_4 .

On the other hand, this technique provides considerable sensitivity, about 50 mV per % v/v.

4.2 Constant bridge voltage heating (figure 6) : remote mine gas detector CTT63/40, multifunction mine gas detector GTM67A

During a measurement, voltage at the terminals is adjusted to 1300 V.

If gas is oxidized on the detector, R_d increases, thus I decreases and U_a increases.

The temperature increase of the filament in the gas is less than in the constant current technique, since the heat added by the oxidation reaction lead to a decrease in those supplied by the current which decreases.

Similarly, when the filament wears, R_d increases but I decreases. Detector temperature increases as the filament wears, but less than in the constant current technique.

4.3 Constant partial voltage heating (figure 7) : remote mine gas detector MT85, multifunction mine gas detector GTM741

The potential differences at the terminals of the compensator and detector filaments are held constant. The potential difference at the terminals of the two filaments mounted in series is adjusted to 1.300 V.

A potential limiting circuit prevents U_a from exceeding 0.760 V by shunting a current (I_{meas}) when R_d increases

The decreased current in the detector attenuates the temperature increase caused by gas oxidation or filament wear. The effect is more pronounced than in the case of the constant bridge voltage set-up.

Increased measurement capacity is partially due to the reduced heating time, brought down to 1.3 seconds (in order to enable the measurement to be read, a circuit keeps the measurement in memory during filament extinction).

The intensity of the heating current, high at the beginning since the filaments are cold, enables operating temperature to be reached in about 1 second (figure 8).

The measurement signal is memorized during the last 300 ms.

Characteristics of the GTM741 mine gas detector using this technique :

- Measurement rhythm : 15 s,
- Sensor lifetime : 1 year,
- Response time : between 15 and 30 s,
- Calibration frequency : weekly.

4.4 Heating by rapid temperature rise and constant detector filament resistance (figure 9) : GTM90C mine gas detector

The increase to operating temperature occurs very rapidly by a constant high intensity current. When this temperature is reached, a circuit maintains the resistance at R_d (1000°C) regardless of gas concentration, by acting on current intensity : if additional heat are supplied by the oxidation of a gas, the circuit decreases the Joule effect heat by reducing the current.

$$R_d(T) = R_1 \times R_3/R_2$$

Temperature rise of the filament lasts 0.2 s ; $I = 1.4$ A (figure 10).

When $R_d(T) = 1.03 \Omega$, the controller reduces intensity in order to maintain R_d at this value.

Variations of the plateau potentiel U_d is the measurement signal. The measurement is memorized before the current is cut.

This heating technique confers a very long lifetime on the sensor : 10,000,000 measurements and independent of the quantities of gas oxidized by the filament. This is due to 3 factors :

- reduced heating time,
- temperature control during measurements,
- slight decrease in filament temperature as it wears: with increasing wear, $R_d(0^\circ\text{C})$ increases. Since $R_d(T)$ remains constant (1.03Ω) filament temperature decreases.

Wear is independent of the gas history of the filament. In this case, it depends only on the number of measurements, which enables zero drift to be simulated in order to carryout an automatic correction and thus considerably reduce maintenance operations.

Consumption is very low as a result of the short heating time and the suppression of the compensating filament.

Comment: the compensating filament can be replaced by a low consumption temperature sensor (thermistor, semiconductors, etc.). Although changes in relative humidity are not compensated, their influence on measurements remains negligible, since they are lower than 0.1% v/v CH₄ at 80% R.H.

The "removal of doubt" at high methane concentrations, which was assured by the compensator and made indispensable by the low measurement rhythms in the initial methane detectors, can be replaced by a "locking" alarm circuit, as in continuous measurement explosimeters.

A practically continuous measurement rhythm of 5 seconds leads to a consumption of 0.024 Joule, *i.e.* a mean current of 0.07 A.

The device requires a power supply higher than 1.2 V. A 2-element 2.5 V nickel-cadmium battery is sufficient.

Characteristics of the GTM90C mine gas detector using this technique :

- Measurement rhythm: 5 s, automatically increases to 2.5 s if the concentration increases,
- Sensor lifetime : 19 months,
- Response time : 15 to 18 s,
- Response time for the alarm to an explosive concentration : < 5 s,
- Consumption : 0.09 A (0.02 A for the electronic circuits),
- Automatic zero correction : every month.

4.5 Summary table

Table 1 (see appendix) summarizes progress in the characteristics and performance of the different techniques.

5. Conclusion and perspectives

The properties of the platinum filament sensor, designed 30 years ago for mining applications, are today optimally used as a result of the perfected conditioning of its power supply. At a similar response time, its electrical consumption is lower than that of low consumption catalytic pellets.

Its high operating temperature effectively protects it against certain catalyst poisons.

Its field of application now extends to industrial and domestic gas detection. The technique of heating by short pulses, specific to the filament with low thermal inertia, enables the principle faults of catalytic oxidation to be overcome, with several improvements: measurement range limited to the stoichiometric value of the air-gas mixture, and absence of selectivity.

Examples :

- 0-100% v/v methane detector (figure 11a)

The heating pulse is decomposed into two temperature plateaus :

- 1st plateau at $T < 400^{\circ}\text{C}$: the filament operates as a hot wire detector and furnishes measurements of concentrations higher than stoichiometry,
- 2nd plateau at 1000°C : the filament gives the measurement of concentrations lower than stoichiometry.

The zero of the hot wire detector is done automatically each time the measurement is lower than the L.I.E.

- Identification of the gas (figure 11b)

The catalytic activity of a combustible gas or vapor as a function of oxidation temperature follows a law specific to each species. The combustible product can be identified by measurements made at different temperature plateaus.

Zeros at the 3 temperatures are done automatically when the air is pure.

INERIS (Institut National de l'Environnement Industriel et des Risques) develops these new techniques involving signal processing and algorithm execution, and is continuing work on the platinum filament sensor in order to improve its performance characteristics ; thus, a new smaller one, to reduce response time, is being developed.

The sensor and the methane detectors described in this document are manufactured by Oldham-France under an INERIS license.

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Legends

Fig. 1. Platinum filament sensor

Fig. 2. Distribution of the filament temperature

Fig. 3. Removal of doubt

Fig. 4. Response time

Fig. 5. Constant intensity heating device

Fig. 6. Constant bridge voltage heating device

Fig. 7. Constant partial voltage heating device

Fig. 8. current shape

Fig. 9. Constant resistance heating device

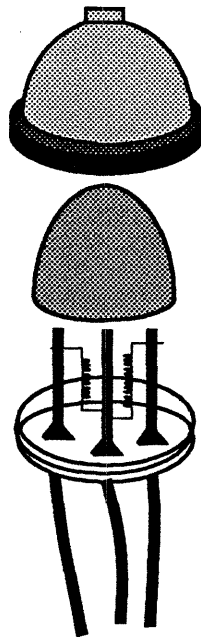
Fig. 10. signals shape

Fig. 11a. 11b. Heating pulses

Appendix - Table 1. Summary table

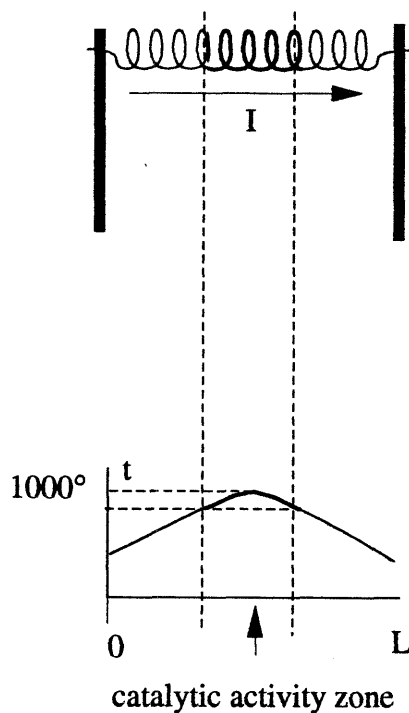
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figure n°1



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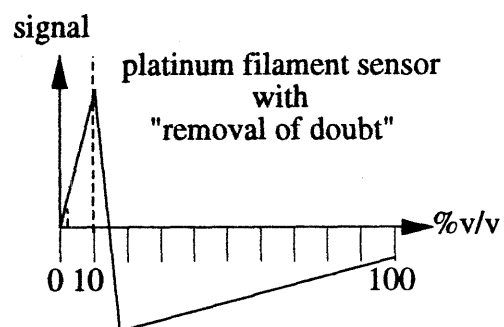
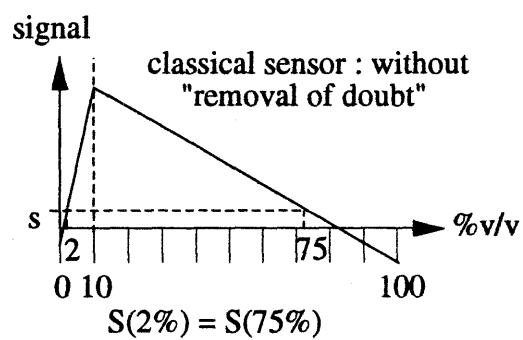
figure n°2



- $R_d(t^\circ) = R_d(0^\circ) \times (1 + kt^\circ)$
- $t^\circ = f(I ; \%v/v \text{ CH}_4)$
- t° = mean temperature of the filament
- $t_{\text{mean}} = \frac{1}{L} \int_0^L t \, (dl)$
- R_d = resistance of detector filament at t°
- $k = 0.004$ for the platinum
- $R_d(0^\circ)$ = resistance at $0^\circ = \rho \times L / S$
- ρ = resistivity ; L = length ; S = section
- $R_d(0^\circ) = 0.35 \, \Omega$ $R_d(1000^\circ) = 1.03 \, \Omega$
- $R_d(1000^\circ) = 1000^\circ$ on the central spire.

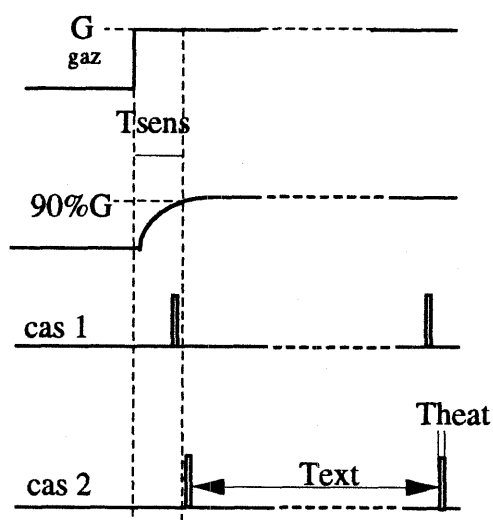
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figure n°3



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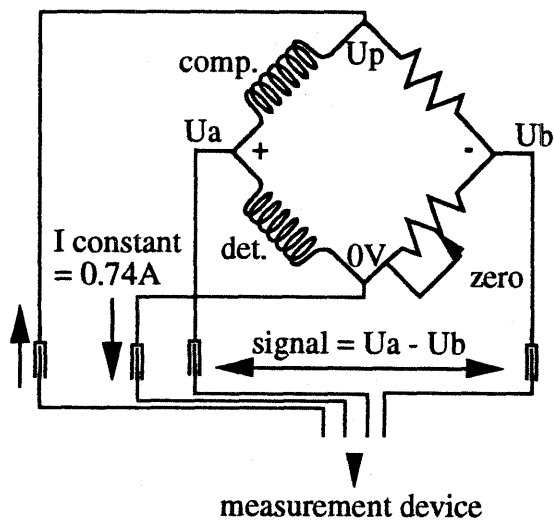
figure n°4



cas 1- response time = $T_{\text{sens}} + T_{\text{ext}}$
cas 2- response time = T_{sens}

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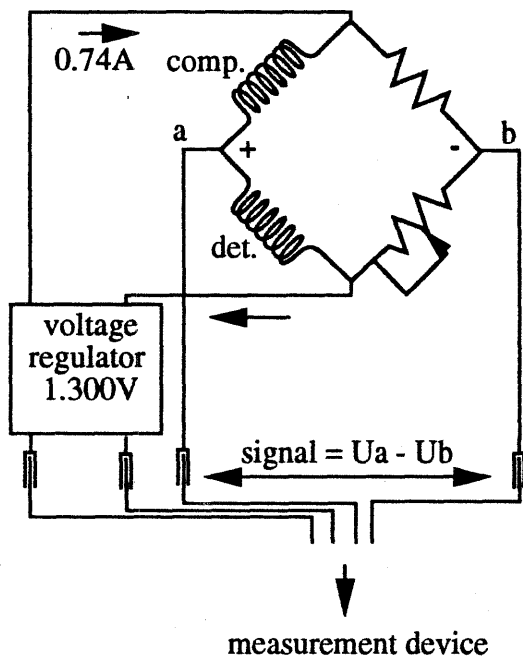
figure n°5



- signal = $50\text{mV} \times \%v/v \text{ CH}_4$
- $T_{\text{heat}} = 3 \text{ s}$
- $W_{\text{meas}} = 2.9 \text{ J}$
- life time :
 - . in air = 100,000 measurements
 - . in 2% CH_4 = 30,000 measurements
- $R_d(2\%) = 1.15 \Omega$

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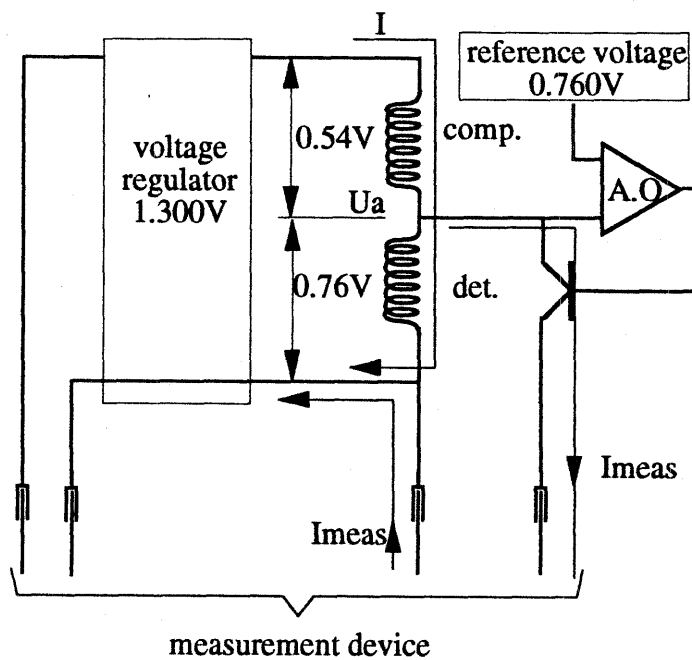
figure n°6



- signal = 20mV x %v/v CH₄
- T_{heat} = 3 s
- W_{meas} = 2.9 J
- life time :
 - . in air = 250,000 measurements
 - . in 2% CH₄ = 100,000 measurements
- R_d(2%) = 1.12 Ω

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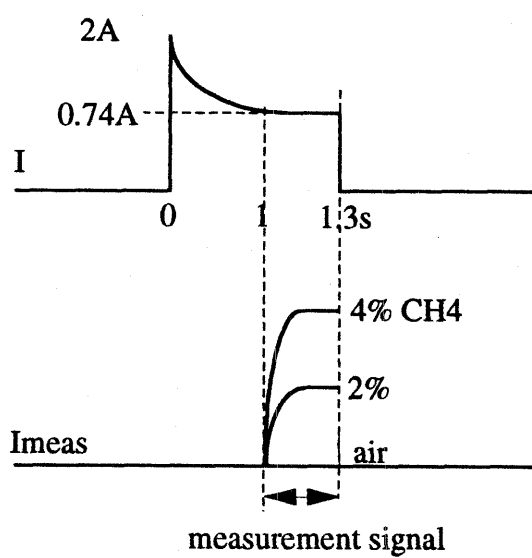
figure n°7



- signal
= $0.015A \times \%v/v CH_4$
- $T_{heat} = 1.3 \text{ sec.}$
- $W_{meas} = 1.25 \text{ J}$
- life time :
 . in air =
 2,000,000 measurements
 . in 2% CH_4 =
 1,000,000 measurements
 $R_d(2\%) = 1.08\Omega$

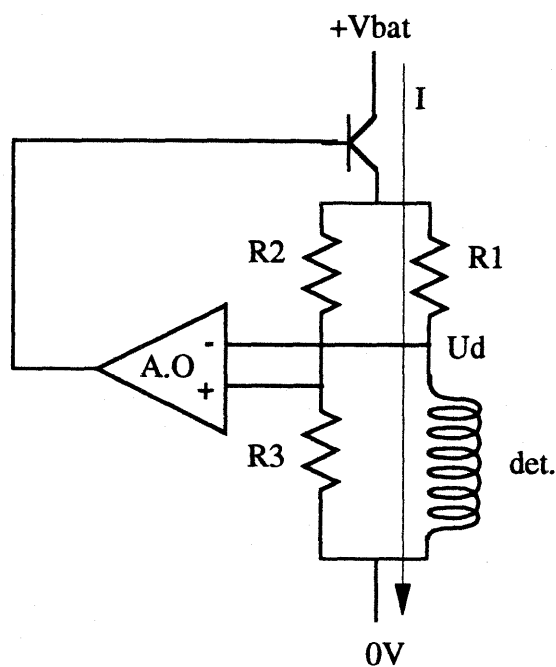
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figure n°8



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figure n°9



- signal = $20\text{mV} \times \%v/v \text{ CH}_4$

- $T_{\text{heat}} = 0.35 \text{ sec.}$

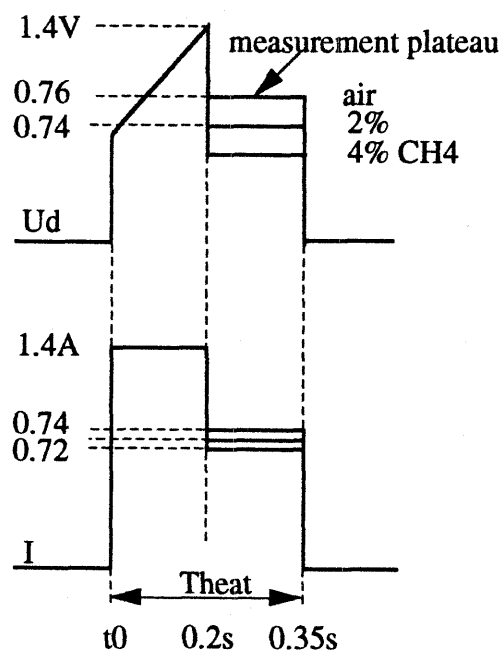
- $W_{\text{meas}} = 0.36 \text{ J}$

- life time in air and in gaz = 10,000,000
measurements

- $R_d(\text{air and gaz}) = \text{cte} = 1.03\Omega$

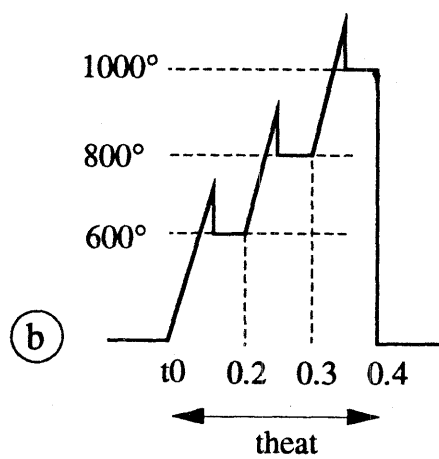
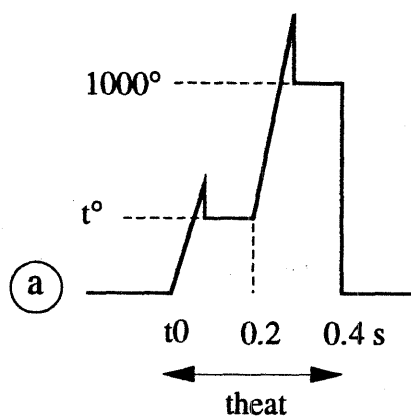
the compensator filament is not used

figure n°10



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figure n°11a - 11b



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Appendix - Table1

| | | d.d.p. at terminals detector filament (Volt) | intensity through the filament (Ampère) | filament resistance (Ohm) | consumption during the measurement (Joule) | life time or capacity of measurements |
|--------------------------------|-----------|--|---|---------------------------------|---|--|
| constant intensity | air | 0.76 | 0.74 | 1.03 | 2.9 | 100,000 |
| | CH4 2% | 0.86 | 0.74 | 1.15 | | 30,000 |
| constant bridge voltage | air | 0.76 | 0.74 | 1.03 | 2.9 | 250,000 |
| | CH4 2% | 0.80 | 0.72 | 1.12 | | 100,000 |
| constant partial voltage | air | 0.76 | 0.74 | 1.03 | 1.25 | 2,000,000 |
| | CH4 2% | 0.76 | 0.71 | 1.08 | | 1,000,000 |
| constant resistance | air | 0.76 | 0.74 | 1.03 | 0.36 | 10,000,000 |
| | CH4 2% | 0.72 | 0.70 | 1.03 | | 10,000,000 |